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APPLICATION OF CHLOROSILANE FINISHES
TO GLASS FIBERS USING THE AZEOTROPIC
DISTILLATION METHOD

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APPLICATION OF CHLOROSILANE FINISHES TO GLASS FIBERS
USING THE AZEOTROPIC DISTILLATION METHOD

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ABSTRACT: The tendency of certain solvents to form low-boiling mixtures (azeotropes) with water was investigated as a means by which to strip surface adsorbed water from glass fibers prior to treatment with NOL-24, a chlorosilane. Neither the loading of finish on the fabric or the effectiveness of the treatment correlated with the presumed different stripping powers of the solvents tried. Results with chloroaromatic solvents indicated that they have substantial potential in the development of an effective, non-aqueous, large-scale process for applying chlorosilane finishes to glass fiber reinforcement.

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AZEOTROPIC DISTILLATION METHOD

Research reported herein was performed under Polaris Research Task PR-4. A method was studied to achieve reproducible and controlled loading of NOL-24 finish on glass fabric used in reinforced plastics. The data were inconclusive, particularly with regard to theory. They show, however, that there is a considerable effect, depending upon solvent used, on two strength properties of laminates made from the treated fabric. This work strongly indicates that an optimized treating process based on chloro-aromatic solvents could be the basis for a non-aqueous commercial organo-chlorosilane finishing system that would give treatments substantially better and more reproducible than now obtained.

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By direction

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INTRODUCTION

1. Glass reinforced plastics with improved strength properties are needed for ordnance of the future. Their high strength-to-weight characteristics have already led to their extensive use in rockets and missiles. However, based on glass filament properties, improved strengths are still possible.
2. A number of factors over the past few years have led to improvements in the strength characteristics of these materials. The development of epoxy laminating resins was a great forward step. Improved laminating techniques, as well as new epoxy curing agents, have resulted in stronger glass fiber-resin composites. Dramatic improvements in laminate strength properties have been realized from new treatments of the glass fibers, which presumably lead to better bonding between the glass and the cured resin. While much progress has been made in glass fiber treatments, there is reason to believe that the end is not in sight and that further substantial improvements in laminate strength properties can still be made.
3. This Laboratory was involved several years ago in a study to develop chlorosilane treatments for glass fibers, which would give improved laminate strengths, particularly in a wet environment. A total of 38 such finishes were synthesized, applied to glass fabric and evaluated in laminates with several thermosetting resins (ref. (a), (b) and (c)). The NOL-24 finish, which is now well known, was one of these finishes (ref. (d)).
4. A study of the effect of a large number of variables in the synthesis and application of the NOL-24 finish was made prior to its release to pilot plant production. The finish was almost lost in the early experimental stages due to working at too high concentrations of the chemical in the solvent used. Some of the other parameters studied involved temperature of the treatment, length of time of the treatment, solvent used, storage history of the glass fabric prior to treatment, manner of carrying out the water scrubbing, and details of the preparation of the finish chemical. At the time of the pilot plant treatment, it was known that dry xylene was a satisfactory solvent and that the concentration of the chemical in this solvent should be between one-half and one per cent. It had also been shown that the NOL-24 chemical taken to 125 to 130% completion, based on moles of hydrogen chloride evolved per mole of each of the starting materials, was satisfactory. There was some evidence based on limited data that better laminate strengths would result if the fabric was conditioned by heating in a stream of dry nitrogen prior to the NOL-24 treatment.
5. There are still many aspects of the NOL-24 treatment, or perhaps of any chlorosilane treatment for glass reinforcement, which are not understood. Laminate strengths from pilot plant NOL-24 treated fabric were in many cases substantially higher than could be realized from laboratory

treated fabric using the same lot of chemical. This was confusing at the time, since there were very few elements in the pilot plant process which could be controlled with a degree of precision comparable to the laboratory process. In fact, this work was carried out on treating equipment which was designed for the application of aqueous base finishes. No attempt was made to engineer a process which would be suitable for an organic solvent system.

6. The subject of this report is the study of a method to control in a reproducible manner the amount (loading) of NOL-24 finish on glass fibers. The method is based on control of glass surface moisture using principles of azeotropy, which can readily be translated into an industrial process for the solvent application of, perhaps, any organochlorosilane finish to glass fiber reinforcement.

7. The results show that azeotropic solvents can be used to strip water from glass fiber surfaces and that the amount of water removed is, in general, dependent upon the boiling point of the solvent. Data from laminates made with cloth which had been treated with NOL-24 under the various experimental conditions show that generally higher flexural strengths are obtained when the higher boiling point solvents were used. There were, however, exceptions. Compressive strengths did not follow the expected trend to higher strengths with progressively higher boiling point solvents. Chlorinated aromatic solvents in some instances, for reasons apparently unrelated to boiling point, were found to lead to very good laminate compressive strength properties. The overall results indicate that xylene was not the best solvent choice for the pilot-plant application of the NOL-24 finish.

THEORY

8. This study is based on an attempted exploitation of one part of the theory of what is believed to occur when chlorosilanes react with glass surfaces. In order to understand the reasoning behind the work reported here, a discussion of the Chemical Bonding Theory will be given.

9. Prior to this work, a theory had been proposed to account for the unusual improvements in polyester laminate strength properties from treatments of glass fabric with vinyltrichlorosilane (ref. (e)). The theory, called the Chemical Bonding Theory, postulated that the vinyl group in the finish on the glass surface could coreact with unsaturated (olefinic) groups in the polyester resin during cure and thus bridge the resin-finish interface with primary chemical bonds. The NOL series of silane finishes were all designed to contain organic functional groups which could, on the basis of this theory, be active sites for bonding to the various resins to be considered. The NOL-24 chemical is the product from the reaction of equimolar amounts of allyltrimethylchlorosilane and resorcinol. This finish when properly applied to glass fabric was found to be very effective with polyester, epoxy, phenolic and melamine laminating resins (ref. (d)).

10. A mechanism has also been postulated for the attachment of chlorosilanes to glass surfaces. It has been shown that these surfaces are covered with a film of water up to 100 molecules thick, this thickness depending upon the humidity of the surroundings (ref. (f)). Certain chlorosilanes are reported to react with this water, molecule for molecule, such that the entire water film is ultimately replaced with a siloxane film (ref. (g)). Apparently this adsorbed water is necessary for effective attachment of chlorosilanes to glass since completely dry glass, which has been baked-out in vacuum, does not become water repellent (hydrophobic) by a treatment with dimethyldichlorosilane (ref. (h)). Siloxane (silicone) films on glass surfaces resulting from exposure to chlorosilanes cannot be removed by neutral solvent extraction and appear to be chemically bound to the surface (ref. (f)). If all the preceding postulates are correct, then chlorosilane base finishes with organic functional groups capable of reaction with laminating resins should serve as a means or mechanism for joining the resin-glass interface with primary chemical bonds.

11. Assuming that NOL-24, essentially a dichlorosilane, would react like dimethyldichlorosilane (DMDCS), the amount of finish per unit area of glass surface would be dictated by the amount of prior adsorbed water on the glass (ref. (g)). The implication here is that a large amount of adsorbed water would lead to a heavy (thick) loading of finish. There is, of course, the possibility that the NOL-24 molecules, being larger than the DMDCS molecules, can react only with a few of the outer layers of water molecules. In this case, the finish would be bonded to some one of the many remaining layers of water molecules which are apparently strongly bound to the glass. It is reasonable to believe that there is an optimum loading of finish. It is also reasonable to believe that it would be undesirable under any circumstances to bond a silicone finish to a water layer even though it is strongly adsorbed to the glass surface.

12. This study is concerned with the exploration of a method, based on the above theory, to control in a reproducible manner the amount of adsorbed water on the glass surfaces prior to the chlorosilane treatment. Some, and perhaps an optimum amount of, adsorbed water is needed in the proposed mechanism to explain the bonding of chlorosilanes to glass (ref. (h)). On the other hand, it has been shown in this laboratory that glass fabric which is exposed to very high humidity prior to treatment gives an inferior NOL-24 treatment.

13. The manner in which water molecules are adsorbed to glass surfaces may be likened to the model for multimolecular layer gas adsorption which has been proposed by Dr. P. H. Emmett (ref. (i)). His discussion suggests that successive layers of gas adsorbate (L) each have their characteristic heat of adsorption (E). It is reasonable to suppose that the heat of adsorption E_1 for the first layer L_1 is greatest; also $E_2 > E_3 > E_4 \dots > E_n$ for $L_2, L_3, L_4 \dots L_n$, respectively. The energy of desorption for a given adsorbed layer should be at least as great as the energy of adsorption. These should accordingly be different for the successive layers and least

for the layers furthest from the adsorbent. The total energy to desorb a given layer would also involve an energy of activation, which for each layer might also be different.

14. There are several ways in which glass fabric could be conditioned, using heat, desiccants, and vacuum, or combinations of these to achieve a controlled and reproducible amount of surface adsorbed water. Such methods might, however, require long times to achieve equilibrium, since glass fabric as usually supplied for finishing comes in tightly wound rolls containing up to 400 yards. There would also be a problem of transferring these rolls of fabric from the conditioning environment to the treating baths without disturbing the surface-moisture equilibrium. Dry glass surfaces pick up moisture very rapidly and hours or days of conditioning could be undone in minutes by exposure to moist air.

15. Distillation using azeotropic (Greek: to boil without change) solvents is another well known way to extract small amounts of moisture from systems which hold water with great tenacity. Advantage is taken of the fact that many organic solvents form constant boiling mixtures with water. In the case of binary systems, which exhibit positive deviations from Raoult's law, a distillate of constant composition will be obtained at some fixed temperature ($p = \text{constant}$) which is lower than the boiling point of either component (ref. (j)). Upon refluxing a water-containing binary azeotrope-forming mixture, such that the condensate must return across a water trap, it is possible to remove the water from the system. The method is simple, powerful, and yet very mild since the temperatures involved are not high. As an example, the monohydrate of p-toluenesulfonic acid, which is heat-sensitive, can be dehydrated without decomposition by refluxing in benzene using a water trap under the condenser (ref. (k)). Another example is a patented commercial process based on the use of benzene and the azeotropic principle which is used to recover absolute alcohol from the constant-boiling alcohol-water mixture which is recovered in the later stages of the fermentation process. The total number of azeotropic systems known in 1952 was about 14,000 (ref. (l)).

16. Azeotropic distillation using different solvents with a wide range of boiling points should, on the basis of postulated energy considerations within the framework of the Emmett model, afford a precise means of arriving at different fixed residual moisture contents on glass surfaces.

17. In this work the assumption was made that the amount of water which could be stripped from the glass surfaces at equilibrium would increase with an increase in the boiling point of the particular solvent used. After the glass fabric had been "dried" to the particular equilibrium condition, the chlorosilane could be added to the system to complete the treatment in-situ. According to the theory (ref. (g)), the amount of chlorosilane reagent (number of molecules) which can attach to unit area of glass surface is strictly dictated by the number of adsorbed water molecules on this area. The amount (and thickness) of finish per unit

area would, as a result, be subject to control in a precise and reproducible manner using principles which could easily be translated into a commercial process.

EXPERIMENTAL

18. The detailed procedure for carrying out the glass fabric treatments is given in Appendix A. A picture of the apparatus used is shown in Figure 1. Materials used and their sources are listed in Appendix B. Pertinent properties of the seven different azeotropic solvents used are shown in Table 1.

19. The first part of each treatment consisted of leading the condensate from the refluxing solvent, in which a roll of heat cleaned glass fabric was immersed, across a water trap until the distillate was water free. Refluxing was then stopped and the amount of water recovered was noted. The system was then allowed to cool down to about 75°C, at which point a known amount of NOL-24 chemical was added to the warm solvent. The finish was thus applied in situ without fabric exposure to an unknown (and uncontrolled) environment. After about one hour the fabric roll was removed from the reaction vessel and solvent washed to remove the excess (and unreacted) chlorosilane. After overnight drying in open air, the fabric was rinsed with distilled water until the wash water was chloride free and then again dried, which completed the treatment.

20. Epoxy, polyester, and phenolic laminates were made from the treated fabrics according to the procedures listed in Appendix I of NavOrd 6705, which is entitled "Proposed Revision of Specification Requirements for 181 Style Glass Fabric Reinforced Plastics." Evaluation of the treatments was based on flexural and compressive strength values obtained on these laminates. The laminate test methods used are given in Appendix II of NavOrd 6705.

RESULTS

21. The relative stripping power of the seven solvents used is shown in Figure 8. Ethyl benzoate, the highest boiling solvent, removed 0.60 ml of water, which is twice the amount obtained with benzene, which boils at about 80°C.

22. Ultimate flexural strength data from laminates using epoxy resin and fabric from the various experiments is shown in Figure 2. Also included are data from a laminate which was made with fabric where boiling xylene had been used to strip off the water prior to the NOL-24 treatment. Dry flexural strengths varied from about 82,000 to 101,000 psi and wet strengths from about 70,000 to 92,000 psi. Strengths generally tended to increase with boiling point of the solvent used, but there were many exceptions.

23. Figure 3 shows similar data with the polyester laminates. Strengths tend to increase in a fairly uniform manner up through the treatment using p-chlorotoluene, which boils at 162°C. The solvents boiling at 170 and 212°C gave treatments only slightly better than those from the treatment using benzene.

24. Phenolic laminate ultimate flexural strength data are shown in Figure 4. There is a slight trend toward better strengths with higher boiling points. The solvent boiling at 170°C (phenetole) gave the best treatment and dry and wet laminate strengths, respectively, of about 92,000 and 95,000 psi were obtained. Slightly higher wet than dry strengths were obtained with four of the eight solvents tried.

25. Compressive laminate strength data with the epoxy resin are shown in Figure 5. There is no real trend to be seen between solvent boiling point and laminate strength. The chlorobenzene system gave about 20% better results than the next best system.

26. Figure 6 shows compressive strengths from the polyester laminates. The wet strengths are highest from the treatments with solvents in the intermediate boiling range.

27. Compressive strengths from the phenolic laminates are shown in Figure 7. Para-chlorotoluene was unusual in this set, and a wet laminate compressive strength of almost 60,000 psi was obtained. The highest and lowest boiling solvents apparently led to the poorest treatments while the intermediate ones were considerably better.

DISCUSSION OF RESULTS

28. Ethyl benzoate, which has the highest boiling point of all the solvents tried, stripped off 0.60 ml of water from the fabric sample. Knowing the amount of surface area on the fabric treated and assuming that a water molecule occupies 14.8 Å² (ref. (m)), the number of layers of water molecules on the glass surface can be calculated.

29. The amount of 181-112 glass cloth in each treatment was equivalent to a single piece measuring 120" x 38" and weighing 883 ± 4 grams. According to the manufacturer's literature (ref. (n)), this cloth is made from three-end yarn using filament which averages 0.00029" in diameter (225 ECE). There are 204 filaments per end. The cloth construction is 57 yarns per inch in the warp direction and 54 in the fill direction. With this information, it is possible to calculate the total filament surface. A yarn twist contraction factor of 0.98 must, however, be divided into this value to obtain a more accurate surface area. This calculation assumes uniform geometry. The value for the total surface area thus calculated is 1.86×10^{22} Å².

30. The total area of the fiber surface can also be calculated by another method if the density of the glass, the weight of the fabric treated, and the filament diameter are all known. The formula for specific surface (M^2/g) is as follows:

$$M^2/g = \frac{4}{\text{filament dia.} \times \text{density}}$$

E glass has a density of 2.54 g/cc. Assuming an average filament diameter of 0.00074 cm (0.00029"), the total calculated surface for 883 grams of fabric is $1.88 \times 10^{22} \text{ Å}^2$.

31. The specific surfaces obtained by the above calculations were, respectively, 0.211 and 0.213 M^2/g . These values compare with 0.12 M^2/g by silanol titrations, which was obtained by Yates, et al, from DuPont (ref. (o)). Armour Research Foundation found specific surfaces of 0.173 M^2/g by calculation and 0.193 M^2/g by BET (ref. (p)) adsorption for 0.00038" (ECG) diameter roving (ref (q)). These latter values interpolated to 0.00029" diameter filament would give specific surfaces for ECE glass filament of 0.226 and 0.252 M^2/g . It is seen, therefore, that the specific surfaces calculated for the fabric used in this study are considerably higher than those obtained by DuPont but somewhat less than those from the Armour data (extrapolated).

32. In order to calculate the area of a single layer of water molecules represented by 0.60 ml of water, the assumption was made that density of the water was exactly one. Taking 18 for the molecular weight of water introduces a negligible error of less than one part per thousand. The calculation is as follows:

$$6.02 \times 10^{23} \times \frac{0.60}{18} \times 14.8 \text{ Å}^2 = 2.97 \times 10^{23} \text{ Å}^2$$

The number of layers of water molecules on the glass surface is then found by dividing the above value by the total surface area on the fabric treated. Carrying out this calculation shows that the 0.60 ml of water obtained by azeotropically stripping with ethyl benzoate removed 16 monomolecular layers of water.

33. Since all packages had been conditioned to a uniform starting condition prior to being placed in the solvent, the conclusion can be made that benzene, which removed 0.30 ml, stripped off only about 8 of the at least 16 layers present. In the case of anisole, only about five monolayers were removed.

34. The laminate data (Fig. 2) indicated that a satisfactory NOL-24 finish was obtained after the fabric was stripped with ethyl benzoate. According to the theory (ref. (h)), there must, therefore, have been sufficient moisture still present to effect the bonding of the silane finish to the fiber surface. Further, on the basis of theory, it can be concluded that the ethyl benzoate system did not provide sufficient

energy to desorb the innermost water layers according to the model suggested by Dr. Emmett. Even after the ethyl benzoate treatment, there are probably several layers of water remaining on the glass surface. Yates (ref. (o)) reported removing 323 molecules of water per square millimicron of glass surface by heating. About half of these came off between 110° and 150°C, one fourth between 150° and 350°C, and the last fourth between 350° and 610°C. His data indicates that the water removed between 110° and 150°C is "strongly physically bound." The remainder he calls "constitutional water" and probably comes from the condensation of silanol groups which are attached to the surface. A calculation using his data shows that there are about 25 layers of these "strongly physically bound" water molecules. It is, therefore, possible that 8 to 10 monolayers of water remained on the glass surface even after the ethyl benzoate treatment.

35. If the reported fact that dimethyldichlorosilane replaces all of the physically bound water, molecule for molecule (ref. (g)), applies to the dichlorosilane NOL-24, then the amount of finish taken on by the fabric would be about one-third of that without prior moisture stripping by ethyl benzoate. The amount of finish taken up following stripping by benzene would be about two-thirds of the loading expected from treatment of unstripped fabric. The NOL-24 loading following the benzene moisture stripping should, therefore, be roughly twice that following an ethyl benzoate stripping. The loading following the anisole treatment should be about two and one-half times that following stripping with ethyl benzoate.

36. Attempts to determine the amount of finish taken up in each experiment were made but were either unsuccessful or inconclusive. An attempt was made to collect the amount of hydrogen chloride evolved from each experiment following the addition of NOL-24 chemical (Fig. 9). This was unsuccessful due, perhaps, to the following:

a. The amount of hydrogen chloride produced by the reaction of the chlorosilane with the remaining adsorbed water would be slight.

b. Hydrogen chloride is quite soluble in all the solvents used and the amount of solvent was very large in terms of the hydrogen chloride expected. Following this work, a titration method to determine the amount of NOL-24 both in solution and on glass fabric was investigated. Scraps of fabric remaining from six of the experiments were analyzed for the amount of NOL-24 present. The results show no relationship such as would be expected from theory (see Table 1). The loading of finish following the ethyl benzoate (b.p. 212°C) and benzene (b.p. 80.1°C) stripping turned out to be about the same. The loading following refluxing in chlorobenzene (b.p. 132°C) was about four times that of these two, while the loading following refluxing with phenetole (b.p. 170°C) was about 1/10. The titration method has now been refined but no fabric remains from these experiments.

37. An examination of the data in Figures 2 - 7 shows that there is no dramatic effect on laminate strength properties as more powerful azeotropic systems (higher boiling point) are used to condition moisture-wise the fabric prior to the NOL-24 treatments. Figures 2 - 4 show that flexural strength generally increases with an increase in the boiling point of the solvents used. There are, however, several exceptions, such as in Figure 3, where the two highest boiling point systems are about as effective as benzene which has the lowest boiling point in the series. Figures 5 - 7 indicate that the better compressive strengths are obtained from fabrics conditioned with solvents boiling in the intermediate range. The laminate data, therefore, do not, as was expected, provide evidence of an indirect nature to substantiate the theory.

38. The strengths obtained from laminates made from fabric which had been preconditioned in the chloroaromatic solvents were in many cases unusual by comparison with the rest. It is possible that xylene was not the best choice of solvent for the pilot-plant application of NOL-24.

39. There are, perhaps, several explanations for the inconclusive support for the theory as evidenced by the laminate strength data. It was assumed that the moisture stripping power of a given solvent would simply be a function of the boiling point of the pure solvent, which was reasonable on the basis of the model. In Table 1 it is seen that the boiling point of the water-solvent azeotropes do not always follow the trend in boiling point of the pure solvents. For instance (Table 1), the water azeotropes for anisole and p-chlorotoluene boil at 95.5° and 95.0°C, respectively, whereas the pure solvent boiling points are 154° and 164°C in the same order. The solvent series which was selected simply on the basis of boiling points ignores, perhaps, very important chemical differences between the solvents which could be equally important in this type of study. The solvents in this series include aromatics, chloroaromatics, ethers and esters. In view of the known tendencies of ethers, and possibly esters, to invite hydrogen bonding, it is possible that the water was more completely removed from the glass than indicated but could not be quantitatively separated from the solvent condensate. Perhaps a better series to study from the point of view of theory would have been an all-aromatic series or an all-chloroaromatic series. It is also possible that there is a substantial solvent effect in itself in the application of this finish. The dielectric constants and dipole moments for the solvents used are shown in Table 1. No correlation with either of these properties of the solvents and laminate strength was found.

CONCLUSIONS AND RECOMMENDATIONS

40. The results of this study show that varying amounts of moisture can be solvent stripped from glass fiber surfaces using the azeotropic distillation method. The laminate strength data obtained with fabric from the various experiments showed much smaller differences than the measured amount of water which was collected in each case might promise.

On the basis of "hindsight," it is now obvious that a more homologous chemical series could have been selected; at least ethers and esters should have been excluded due to their potential for hydrogen bonding.

41. Despite the inconclusive results as far as theory and its relation to loading of finish is concerned, there is no doubt that the azeotropic principle has potential for quality control in the application of chlorosilane finishes. There is at present no engineered process for the solvent (non-aqueous) application of finishes to glass fabric. With the known deleterious effects of even high humidity to glass fiber strength (ref. (r)), it would not be surprising if an interest in a non-aqueous finishing process will develop. The azeotropic method has no obvious limitations to scaling up to a safe, efficient commercial manufacturing process.

42. Laminate strength values perhaps 20% higher than the best in Figures 2 - 7 have been obtained with fabric finished with NOL-24 using treating methods which were quite crude (ref. (d)). These laminate strengths were not, however, always reproducible. The same methods of treatment often led to results quite inferior to those shown here. It is believed that optimization of an azeotropic method could lead not only to more uniform chlorosilane treatments but to treatments more effective than any found heretofore.

43. The compressive laminate strength data strongly indicate that chloroaromatic solvents have special merit and should be studied further.

TABLE 1
DATA ON AZEOTROPIC SOLVENTS USED

Azeotropic Solvent A	Boiling Point of A, °C	Boiling Point of H ₂ O-A Azeotrope, °C ^{a/}	Weight % of H ₂ O in Vapor ^{a/}	Dipole Moment of A ^{b/}	Dielectric Constant of A ^{c/}	H ₂ O Stripped from Fabric ml ^{d/}	Weight % of NOL-24 Found ^{e/}
Benzene	80.1	69.3	8.83	0	2.12	0.30	0.09
Toluene	111	84.1	13.5	0.40	2.32	0.42	0.29
Chlorobenzene	132	90.2	28.4	1.52	5.97	0.40	0.35
Anisole	154	95.5	40.5	1.20	4.2	0.20	no data
p-chlorotoluene	164	95.0	no data	1.80	5.55	0.50	0.19
Phenetole	170	97.3	59.0	0.70	4.55 ^{d/}	0.50	0.01
Ethyl benzoate	212	99.4	84.0	2.0	6.1	0.60	0.08

H

- ^{a/} "Azeotropic Data," L. H. Horsley, American Chemical Society, 1952
^{b/} Calculated from group moments, Lange's Handbook of Chem., p. 1227
^{c/} Int. Crit. Tables, Vol. 6, pp. 89-94; T °C = 20; audiofrequency
^{d/} Same as c, except at T °C = 21
^{e/} See Figure 7
^{f/} Unpublished NOL data

TABLE 2
FLEXURAL AND COMPRESSIVE LAMINATE STRENGTH DATA SUMMARY^{a/}

Solvent	Average Laminate Strength x 10 ⁻³ psi											
	Epoxy				Polyester				Phenolic			
	Flexural		Compressive		Flexural		Compressive		Flexural		Compressive	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
Benzene	84	78	44	38	79	58	30	28	78	78	43	46
Toluene	91	81	44	43	80	60	39	26	81	78	47	50
Chlorobenzene	100	86	56	51	88	70	43	32	90	90	57	49
Anisole	88	71	44	42	87	69	41	36	81	81	45	49
p-chlorotoluene	87	84	47	47	85	69	42	34	85	85	59	53
Phenetole	94	80	44	41	80	65	43	30	92	95	48	51
Ethyl Benzoate	102	93	49	47	81	64	40	32	91	85	44	43

^{a/} See Figures 2 through 7 for details.

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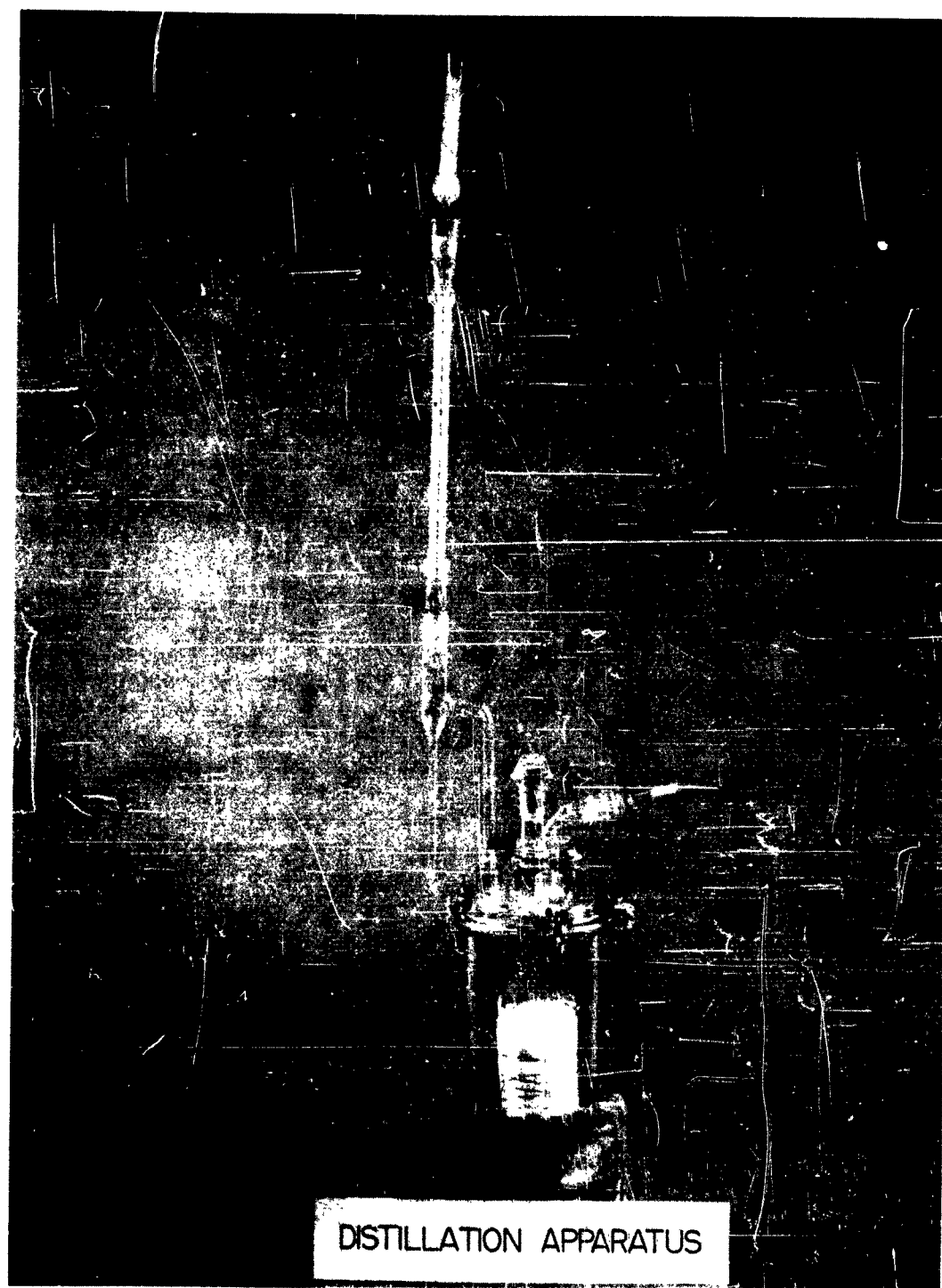
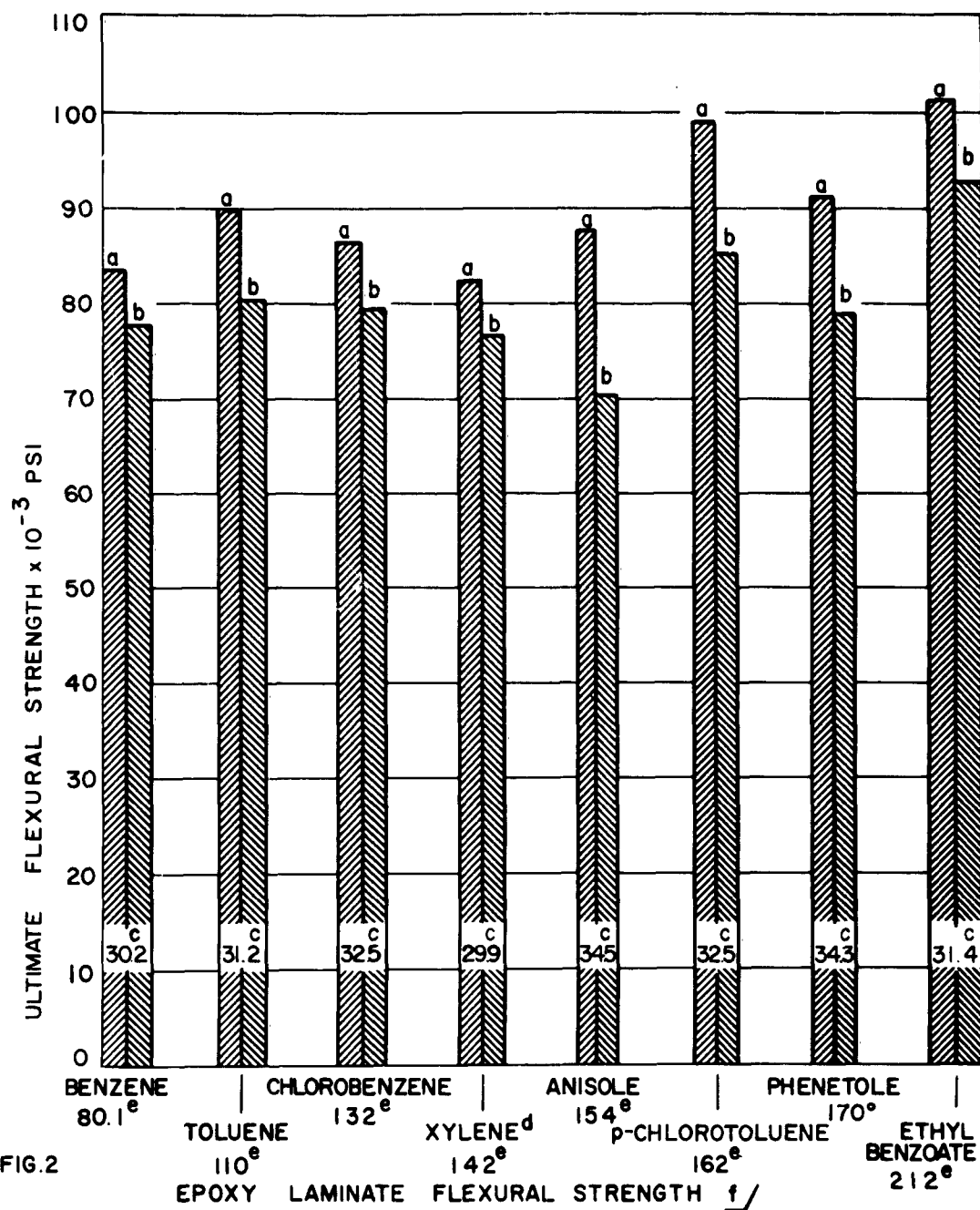


FIG. 1



- a. DRY STRENGTH
- b. STRENGTH AFTER 2 HOURS IN BOILING WATER
- c. RESIN CONTENT, %
- d. A PREVIOUS EXPERIMENT USING BOTH DIFFERENT GLASS CLOTH AND NOL-24 CHEMICAL
- e. BOILING POINT OF SOLVENT, °C.
- f. AVERAGE OF AT LEAST FOUR SPECIMENS

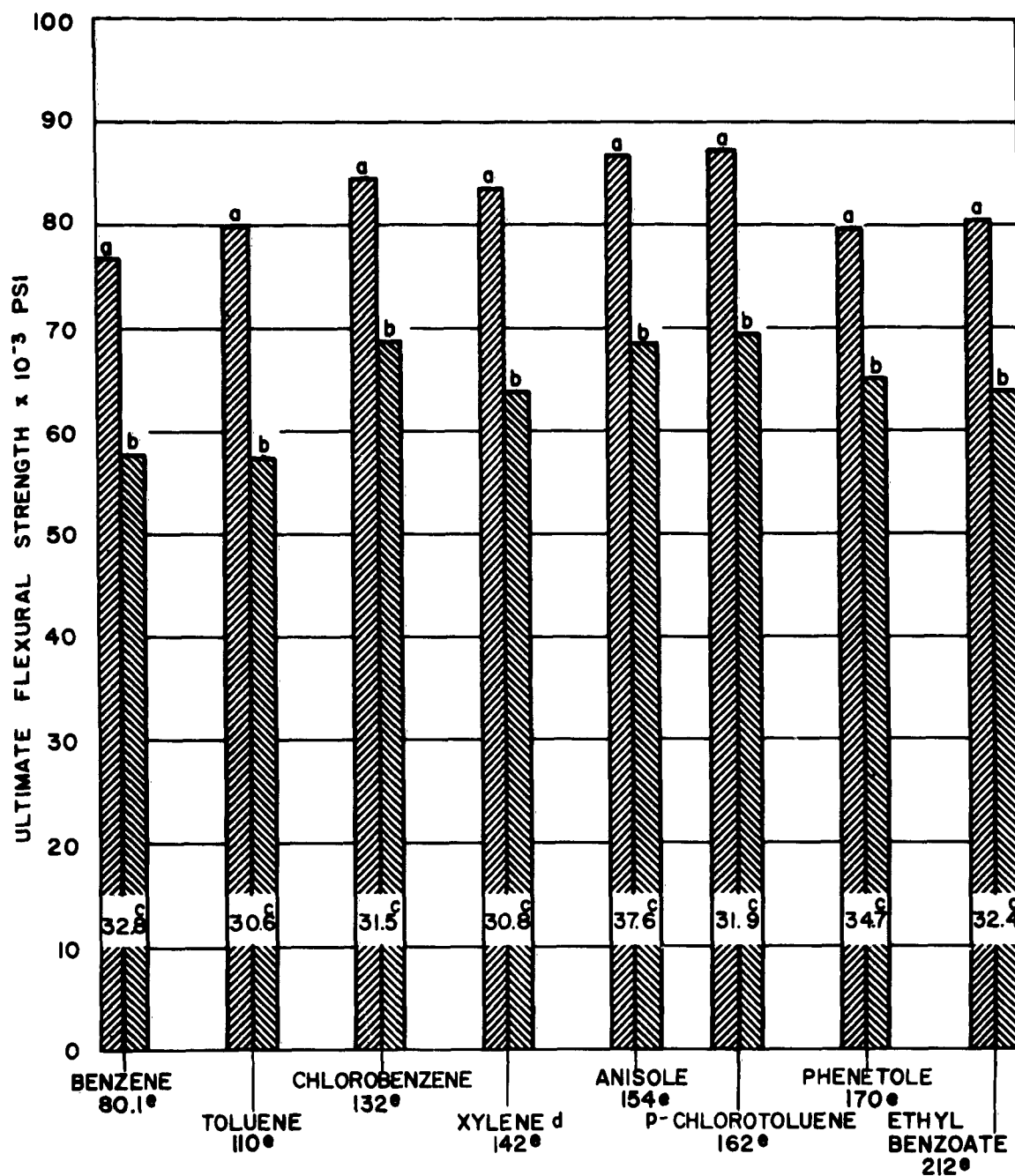


FIG. 3 POLYESTER LAMINATE FLEXURAL STRENGTH ^f/

a. DRY STRENGTH

b. STRENGTH AFTER 2 HOURS IN BOILING WATER

c. RESIN CONTENT, %

d. A PREVIOUS EXPERIMENT USING DIFFERENT GLASS CLOTH AND NOL-24 CHEMICAL

e. BOILING POINT OF SOLVENT, °C

f. AVERAGE OF AT LEAST 4 SPECIMENS

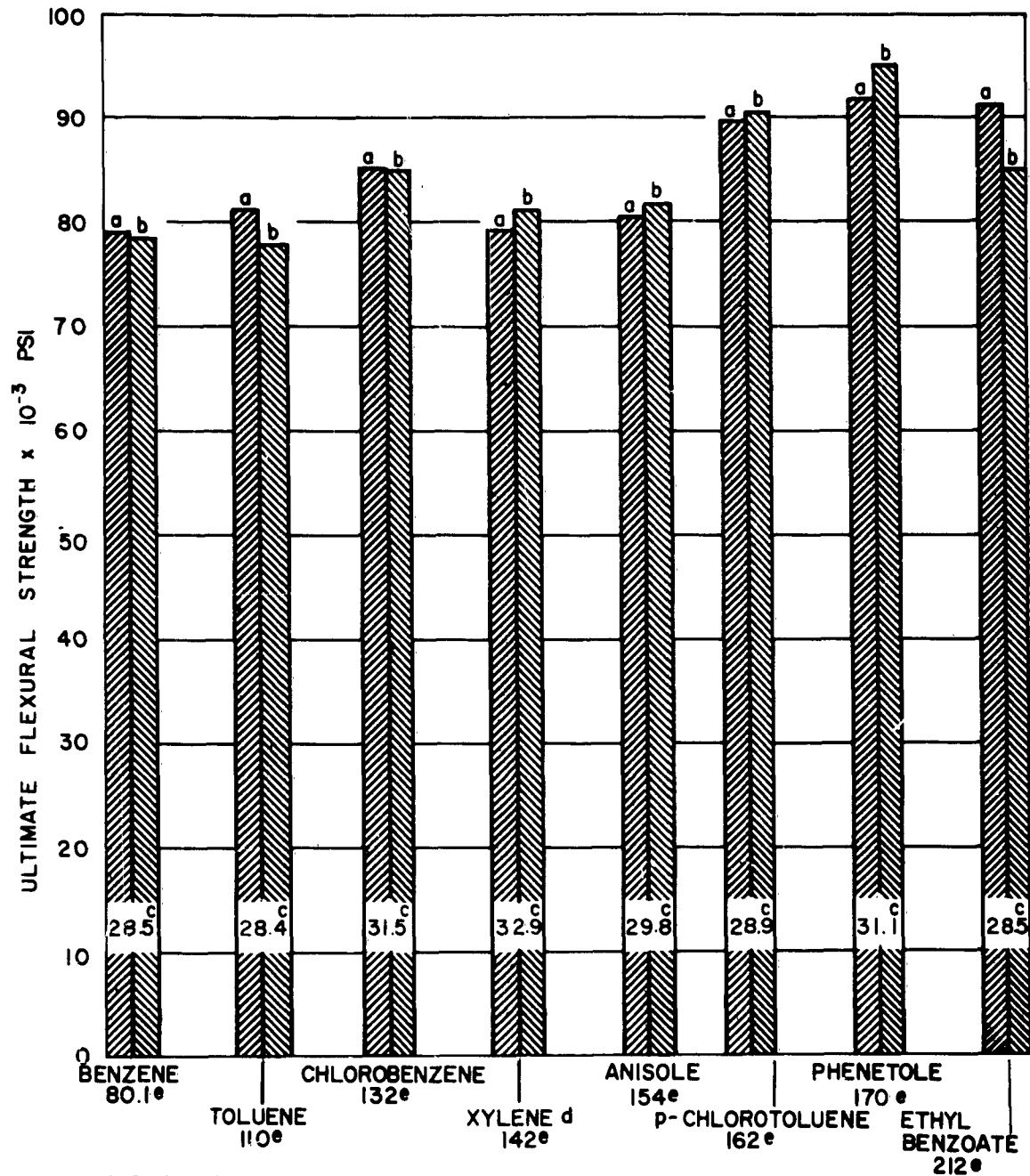


FIG. 4 PHENOLIC LAMINATE FLEXURAL STRENGTH ^{f/}

a. DRY STRENGTH

b. STRENGTH AFTER 2 HOURS IN BOILING WATER

c. RESIN CONTENT, %

d. A PREVIOUS EXPERIMENT USING BOTH DIFFERENT GLASS CLOTH AND NOL-24 CHEMICAL

e. BOILING POINT OF SOLVENT °C

f. AVERAGE OF AT LEAST 4 SPECIMENS

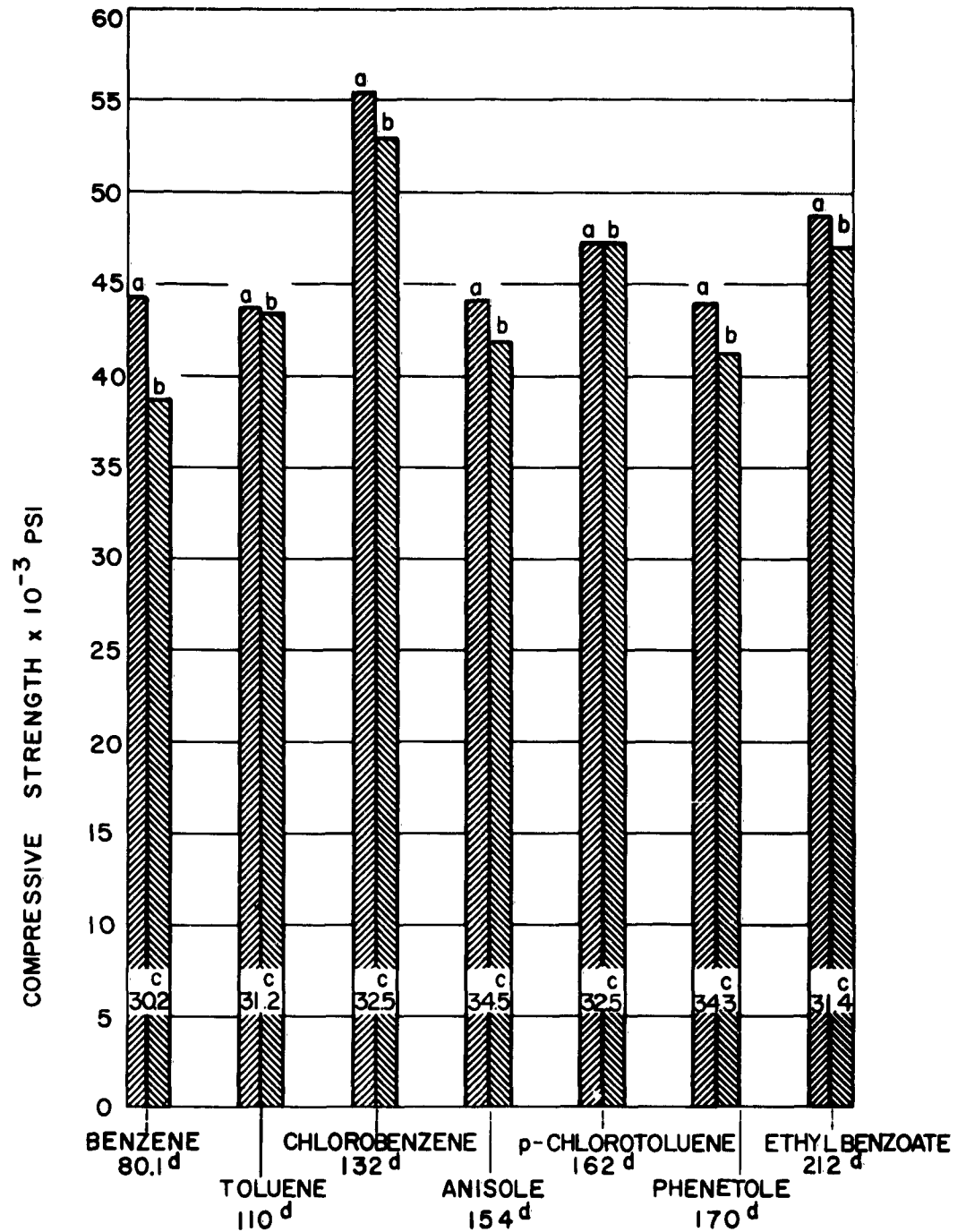


FIG. 5 EPOXY LAMINATE COMPRESSION STRENGTH ^{a/}
^{a.} DRY STRENGTH
^{b.} STRENGTH AFTER 2 HOURS OF BOILING WATER
^{c.} RESIN CONTENT, %
^{d.} BOILING POINT OF SOLVENT, °C.
^{e.} AVERAGE OF AT LEAST FOUR SPECIMENS

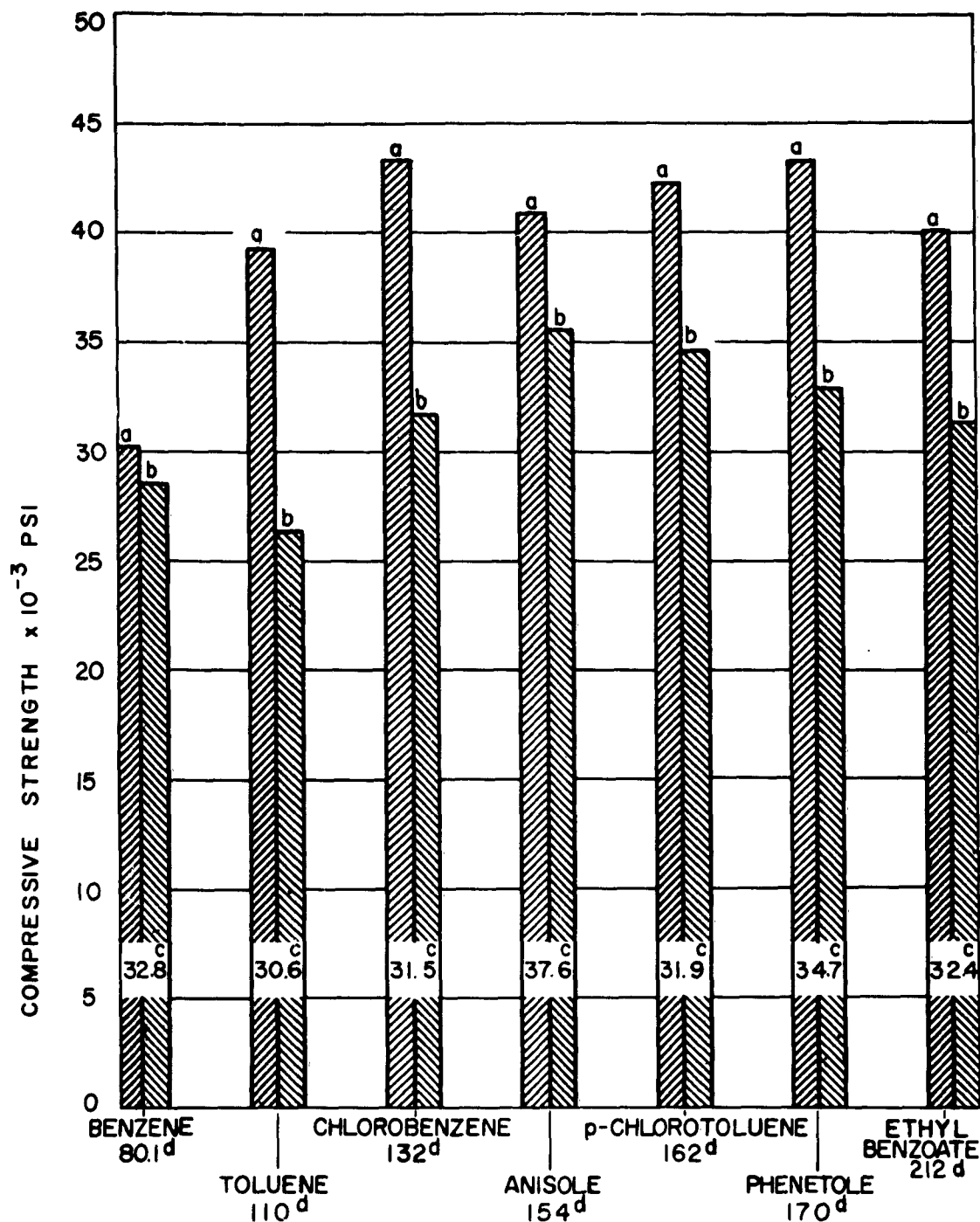


FIG. 6 POLYESTER LAMINATE COMPRESSIVE STRENGTH ^{9/}

- a. DRY STRENGTH
- b. STRENGTH AFTER 2 HOURS IN BOILING WATER
- c. RESIN CONTENT, %
- d. BOILING POINT OF SOLVENT, °C
- e. AVERAGE OF AT LEAST FOUR SPECIMENS

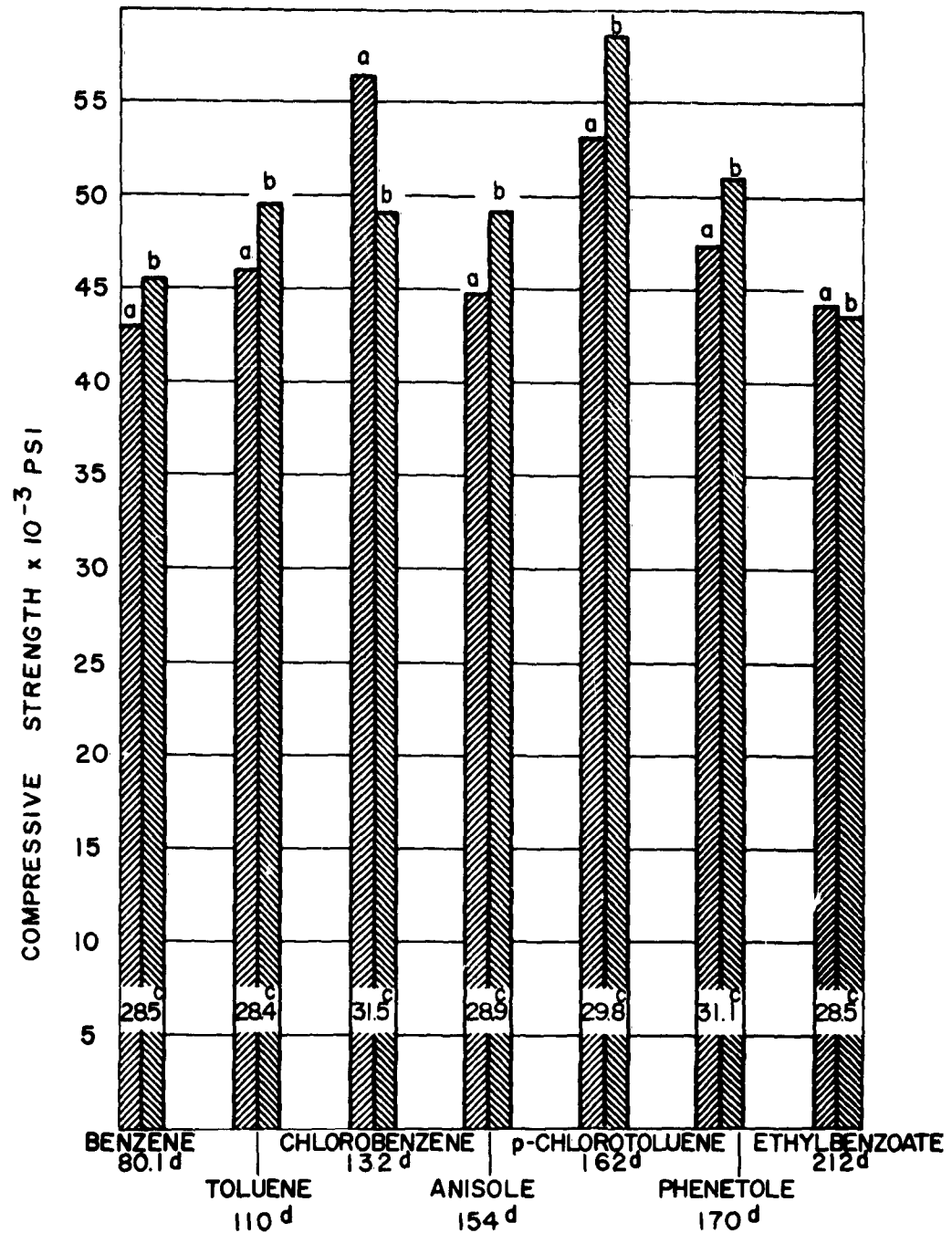


FIG. 7 PHENOLIC LAMINATE COMPRESSIVE STRENGTH

- a. DRY STRENGTH
- b. STRENGTH AFTER 2 HRS. IN BOILING WATER
- c. RESIN CONTENT, %
- d. BOILING POINT OF SOLVENT, °C
- e. AVERAGE OF AT LEAST 4 SPECIMENS

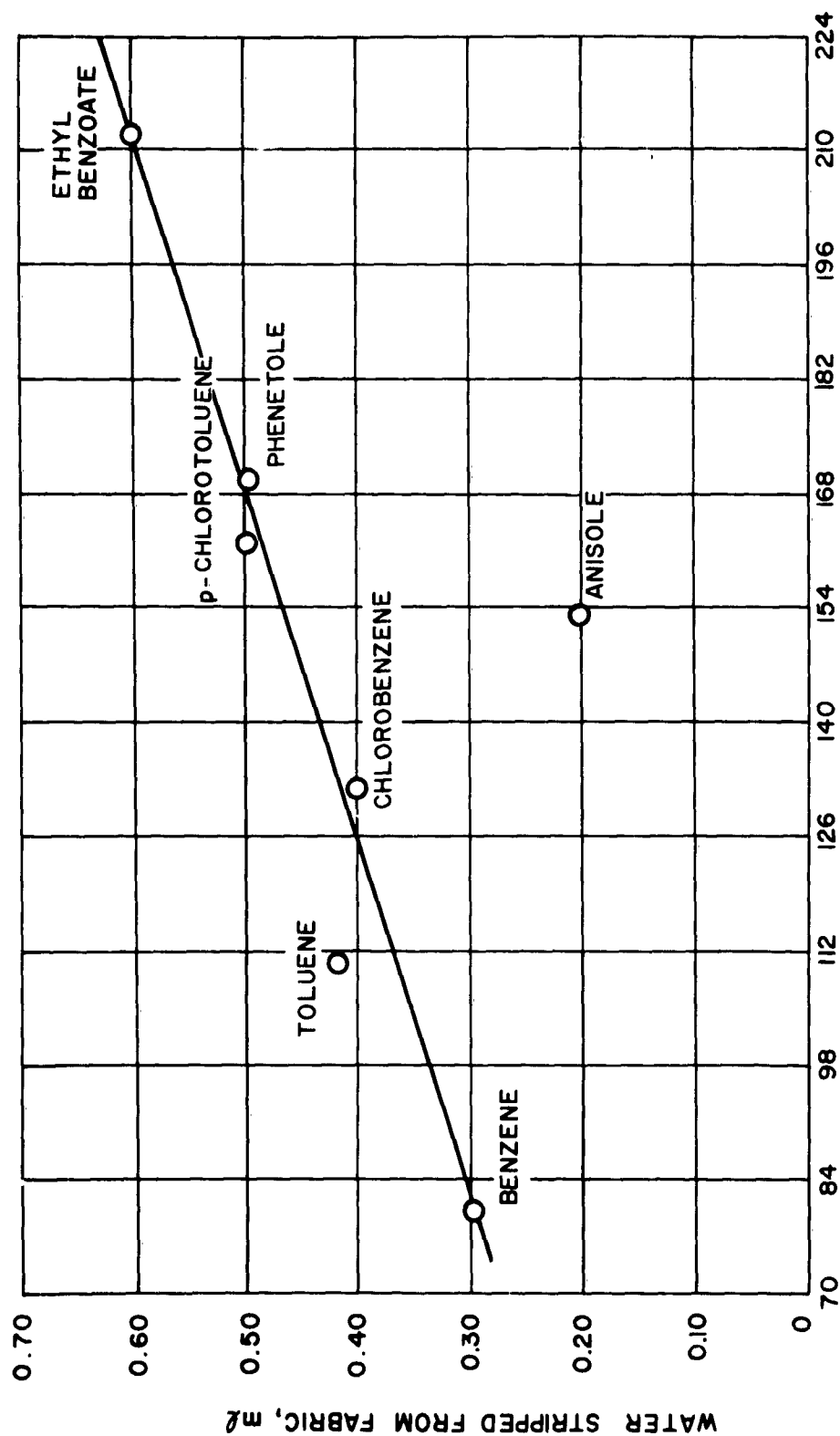


FIG. 8 WATER STRIPPING POWER OF SOLVENT vs SOLVENT BOILING POINT

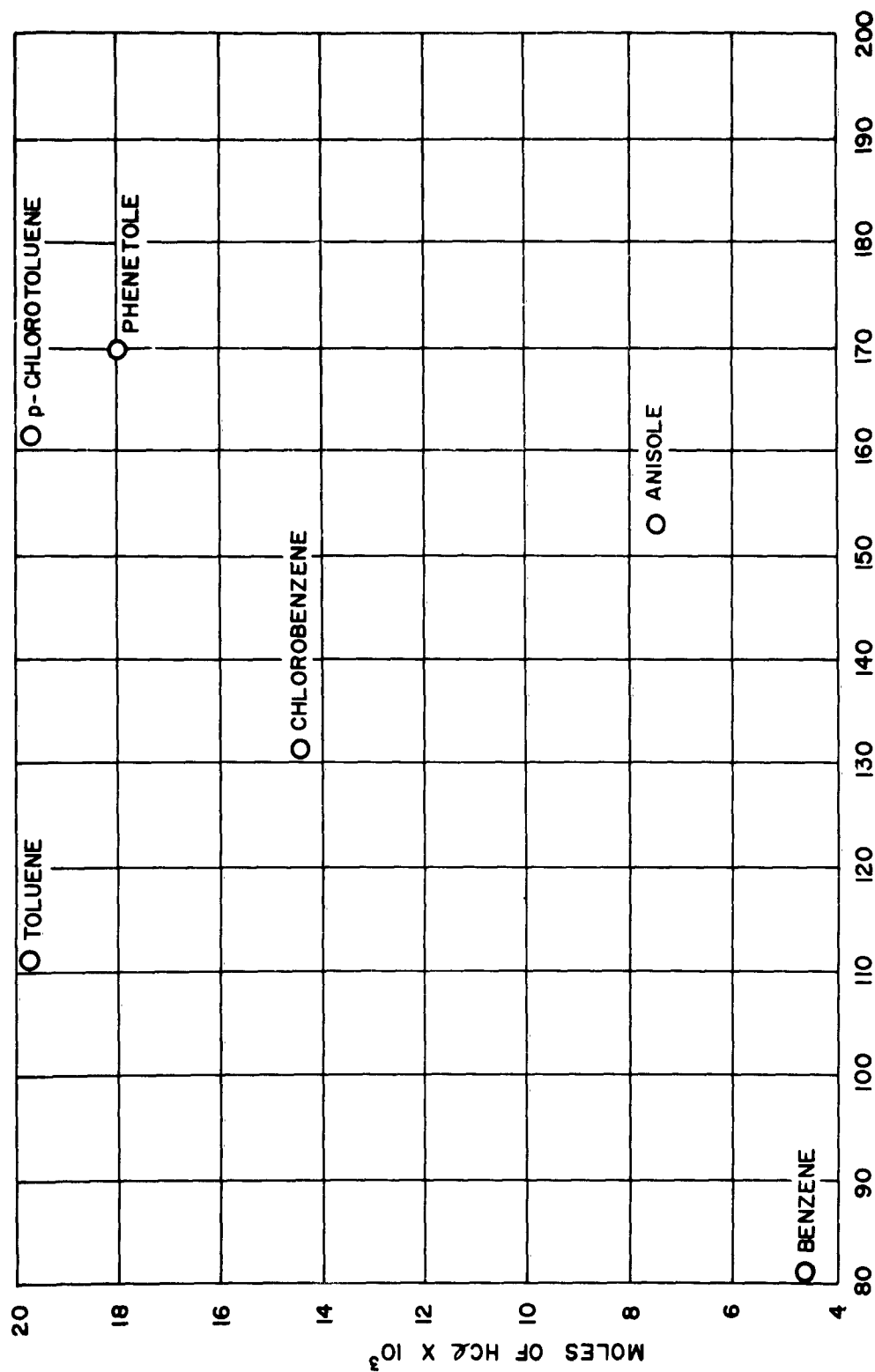


FIG. 9 AMOUNTS OF HYDROGEN CHLORIDE RECOVERED AFTER
NOL-24 TREATMENT^a
^a. DETERMINED AS SILVER CHLORIDE

APPENDIX A

EXPERIMENTAL PROCEDURE

A-1. The apparatus for carrying out the azeotropic distillations is shown in Figure 1. This consisted of a three-liter resin pot which was fitted with a Dean-Stark water trap and a West water-cooled condenser. Heating was accomplished by the use of a "Glascol" mantle, which was energized through a variable voltage supply ("Variac"). To minimize solvent contamination, all ground-glass joints were sealed with minimal amounts of "Nonaq" lubricant (Fisher No. 14-633).

A-2. A large number of strips of 181 style heat-cleaned glass cloth were cut along the fill direction from a single lot (roll) of fabric. These strips measured 38" x 8", the latter dimension being in the warp direction. Fifteen of these strips were rolled up into a compact package about 4 1/2" in diameter. These were securely bound with eight-end glass roving such that the packages could be conveniently handled. About 10 such packages were made up and stored in an oven at $49^{\circ} \pm 2^{\circ}\text{C}$ for three or more days to assure a uniform initial condition. The weights of the rolls were 883 ± 4 g.

A-3. Several holders for the packages were also made up to facilitate handling during the treatments. These holders consisted of 8mm glass rods, 16" long, to one end of which was fused a 3" length of glass rod to form a tee. Prior to a treatment, one of these glass holders was taken into the oven and inserted through the center of the package. The glass fabric roll could as a result be manipulated without contamination and without the package coming apart in the ensuing handling.

A-4. A total of seven different azeotropic solvents with boiling points ranging from 80° to 212°C were chosen for this study. These are listed in Table 1, together with properties pertinent to this work. In addition, a limited amount of earlier similar work with xylene is reported since some laminate strength data were available for comparison.

A-5. The treatments involving the seven solvents were carried out with reagent from a single lot of NOL-24 chemical, which had been found to be of good quality. The concentration used was 0.9% by weight. The treatment with xylene was done with NOL-24 from a different lot, which was also of satisfactory quality.

A-6. At the start of an experiment the resin pot was charged with a known volume varying from 2 to 2.3 liters of the solvent to be used. Smaller volumes were used in the case of the high boiling point solvents, since their volume expansion was considerable. Before heating was started the system was thoroughly flushed with dry nitrogen to remove oxygen which could be presumed to be damaging to the high boiling solvents. After boiling had commenced, the solvent was allowed to reflux for about one-half hour, at which time water had ceased to condense from the distillate.

A-7. Heating was then stopped and the solvent allowed to cool to 50° - 60°C. At this point the water trap was either cleaned out or replaced with a dry one. The resin pot cover was then removed and a package of glass fabric quickly transferred from the oven to the warm solvent. After closing the apparatus, it was again flushed with dry nitrogen. The system was then brought to a boil and allowed to reflux until water ceased to come over. The overall refluxing time was about 3 1/2 hours, but in most cases the system had ceased to yield water in the first half-hour. At the end of this time the amount of water collected was carefully noted to the closest hundredth of a milliliter and the heating stopped.

A-8. The system was allowed to cool to about 75°C, at which time the water trap was removed. The condenser exit was also fitted with a connection to an adsorption train and then set directly into the resin pot cover. A quantity of NOL-24 chemical, sufficient to give the desired concentration, was then added from a dropping funnel. These operations were done in such a manner as to minimize exposure to atmospheric humidity. Dry nitrogen was now introduced under the solvent near the bottom of the resin pot in such a manner as to provide a vigorous agitation. The purpose here was twofold: (a) to assure bringing the NOL-24 chemical to the fabric in every part of the package to get a uniform treatment and (b) to sweep hydrogen chloride out of the solution. An attempt was made to collect and determine the latter by means of a silver nitrate adsorption trap which was connected to the top of the condenser. On the basis of the theory, the amount of hydrogen chloride evolved (and silver chloride precipitated) should be a direct measure of the amount of finish taken up by the fabric (ref. (g)). The agitation with nitrogen continued for one hour during which time the solution was kept at about 60°C.

A-9. At this point the package was removed and most of the solvent allowed to drain out. It was then slipped off the holder and folded into a piece of clean glass cloth. The package, thus protected from being soiled, was centrifuged for about three minutes to remove more solvent and unreacted NOL-24. After this the package was remounted on the glass holder and immersed in dry xylene. It was raised and lowered in this wash solvent several times for a period of about three minutes. The package was again wrapped in glass cloth and centrifuged as before. This procedure was repeated three times and the purpose of it was to remove as completely as possible all excess unreacted NOL-24 reagent. At this point the package was undone and the strips hung up to dry in the open air. The next day the strips were placed for about one-half hour in a porcelain-coated tray containing distilled water. Gentle agitation of the strips in the water assured good washing action. The purpose of this was to hydrolyze all remaining silicon-chlorine bonds and to remove soluble chlorides. One to two additional rinses were carried out until the wash water was essentially chloride free. Following this, the cloth was centrifuged and the strips separately hung up to dry. This completed the treatment.

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APPENDIX B

MATERIALS USED

B-1. The following is a list of the materials used:

181-112 Style Glass Fabric - supplied by United Merchants
Industrial Fabrics, 1407 Broadway, New York 18, New York

Benzene, Fisher No. B-411

Toluene, Fisher No. T-324

Chlorobenzene, Fisher No. B-255

Anisole, Fisher No. A-834

p-Chlorotoluene, Fisher No. 74

Phenetole, Fisher No. 200

Ethyl Benzoate, Fisher No. 112

Xylene, Fisher No. X-5

Epon 828 (epoxy resin), Shell Chemical Company,
380 Madison Avenue, New York 17, New York

Paraplex P-43 (polyester resin), Rohm and Haas Co.,
Washington Square, Philadelphia 5, Pennsylvania

BLL 3085 (phenolic resin), Union Carbide Co., 30 East
42nd Street, New York 17, New York

1,3-diaminobenzene (CL), General Aniline and Film Co.,
435 Hudson Street, New York 14, New York

Lupersol DDM Catalyst, Lucidol Division of Wallace and
Tiernan, Inc., 1740 Military Road, Buffalo, New York

Cobalt Naphthenate (6%), Nuodex Products, Inc.,
Elizabeth, New Jersey

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Glass fibers	GLAC	Loading	LOAD	
Application	APPT	Aromatic	AROM	
Azeotropic	AZTR	Non-aqueous	NONC	
Distillation	DSTI	Reinforced	REIN	
Method	METD	Plastics	PLAS	
Solvents	SOLV			
Low	LOWE			
Boiling	BOIL			
Mixtures	MIXT			

<p>Naval Ordnance Laboratory, White Oak, Md. (MOL technical report 63-1) APPLICATION OF CHLOROSILANE FINISHES TO GLASS FIBERS USING THE AZEOTROPIC DISTILLATION METHOD (U), by Porter W. Erickson and Michael J. McGreal. 28 Jan. 1963. v.p. illus. Task PR-4. UNCLASSIFIED</p> <p>The tendency of certain solvents to form low-boiling mixtures (azeotropes) with water was investigated as a means by which to strip surface adsorbed water from glass fibers prior to treatment with MOL-24, a chlorosilane. Neither the loading of finish on the fabric or the effectiveness of the treatment correlated with the presumed different stripping powers of the solvents tried. Results with chloro-aromatic solvents indicated that they have substantial potential for the development of a non-aqueous process for applying chlorosilane finishes to glass fiber reinforcement.</p>	<p>1. Glass cloth - Coatings Azeotropes Chlorosilanes I. Title II. Erickson, Porter W. III. McGreal, Michael J., jt. author IV. Project Abstract card is unclassified.</p>
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